COLLECTIVE VIBRATIONS OF WATER-SOLVATED HYDROXIDE IONS INVESTIGATED WITH BROADBAND 2DIR SPECTROSCOPY

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The infrared spectra of aqueous solutions of NaOH and other strong bases exhibit a broad continuum absorption for frequencies between 800-3500 cm-1, which is attributed to the strong interactions of the hydroxide ion with its solvating water molecules. To provide molecular insight into the origin of the broad continuum absorption feature, we have performed ultrafast pump-probe and 2DIR experiments on aqueous NaOH by exciting the O—H stretch vibrations and probing the response from 1350-3800 cm-1 using a newly developed sub-70 fs broadband mid-infrared source. These experiments, in conjunction with harmonic vibrational analysis of OH–(H2O)n clusters, reveal that O—H stretch vibrations of aqueous hydroxides arise from coupled vibrations of multiple water molecules solvating the ion. We classify the vibrations of the hydroxide complex by symmetry defined by the relative phase of vibrations of the O—H bonds hydrogen bonded to the ion. Although spectral broadening does not allow us to distinguish 3- and 4-coordinate ion complexes, we find a resolvable splitting between asymmetric and symmetric stretch vibrations, and assign the 2850 cm-1 peak infrared spectra of aqueous hydroxides to asymmetric stretch vibrations.